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SOLID ELECTROLYTIC FUEL CELL

[Abstract]

PURPOSE: To prevent the crack of a solid electrolyte by a thermal distortion by using a seal material in which a specified volume of SnO_2 particles having a specified particle size are added to a glass having specified values of thermal expansion coefficient and melting point.

CONSTITUTION: A seal member 6 is applied to the connecting part between a solid electrolyte 1 and a ceramic tube 3 of different member in a solid electrolytic fuel cell, and the both are sealed and fixed to each other. When a seal member in which 5-40% by volume of SnO_2 particles having a particle size of 10-500μm are added to a glass having a melting point of

800 to 110°C is used as the member 6, the cracking of the solid electrolyte caused by a thermal distortion is prevented.

[CLAIMS]

[Claim(s)]

[Claim 1] A solid electrolyte fuel cell characterized in that a seal member 6 in which 5 to 40% by volume of SnO_2 particles having a particle size of 10 to 500μm are added to a glass having a thermal expansion coefficient more than 2x10-6/°C higher than that of SnO_2 particles and a melting point of 800 to 110°C, is applied to the connecting part between a solid electrolyte and a different member and the connecting part is sealed and fixed.

DETAILED DESCRIPTION

[Title of the invention]

SOLID ELECTROLYTIC FUEL CELL

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to a solid electrolyte fuel cell, and particularly to the sealing of the connecting part between a solid electrolyte and a different members of the solid electrolyte fuel cell.

[0002]

[Description of the Prior Art] The solid electrolyte fuel cell shown in FIG. 1 consists of an electrolyte 1, porous electrodes 2 which were applied to both sides of an electrolyte 1, a ceramic tube 3 for supporting the electrolyte 1, an electric ejection line 4 for to supply power, which is connected to the electrode 2, a gas pipe 5 for supplying and discharging fuel gas to and from the electrolyte 1, a seal member 6 for sealing the fuel gas in a high-temperature section near the electrolyte 1, the rubber plugs 7 sealing the fuel gas in the low-temperature section, the silicone rubber 8, and electric furnaces 9.

[0003] In the conventional solid electrolyte fuel cell, the thermal expansion coefficient of a seal member is similar to that of the electrolyte 1 and the seal member 6 melts at the temperature near the that of the activation of a solid electrolyte fuel cell .

[0004]

[Problem(s) to be Solved by the Invention] In the conventional solid electrolyte fuel cell, although the thermal expansion coefficient of a seal

member 6 is similar to that of the electrolyte 1, the crack of the electrolyte 1 has occurred at the time of cooling due to the stress generated by the slight difference of a thermal expansion coefficient, for this reason there was a disadvantage that the fuel gas may be leaked when the temperature is raised, so that the output of a fuel cell may be deteriorated.

[0005] An object of the present invention is to solve the above-mentioned problems in view of the above-mentioned technical level and to provide a solid electrolyte fuel cell without the above disadvantages that the conventional solid electrolyte fuel cell has.

[0006]

[Means for Solving the Problem] This invention relates to a solid electrolyte fuel cell characterized in that a seal member 6 in which 5 to 40% by volume of SnO_2 particles having a particle size of 10 to 500μm are added to a glass having a thermal expansion coefficient more than 2x10-6/°C higher than that of SnO_2 particles and a melting point of 800 to110°C, is applied to the connecting part between a solid electrolyte and a different member and the connecting part is sealed and fixed.

[0007] As the solid electrolyte used in this invention, generally ZrO_2 can be used, and as a glass having a thermal expansion coefficient more than 2x10-6/°C higher than that of SnO_2 particles and a melting point of 800 to 110°C, the common glass can be used since it has such a property.

[0008]

[Function] After operating a solid electrolyte fuel cell and raising its temperature up to a high temperature (800 to 1100 °C), when it descends

to a room temperature, difference of thermal expansion coefficients among those of a sealing material matrix (glass), a dispersed particle (SnO_2) and a solid electrolyte causes a distortion among them. If the sealing material in this invention is used, the crack generated by the distortion which occurs in a sealing material can be prevented from making a solid electrolyte generate distortion.

[0009] The reason to add a seal member of this invention are added to a glass having a thermal expansion coefficient more than $2x10^{-6}$/°C higher than that of SnO_2 particles (its thermal expansion coefficient: $4x10^{-6}$/°C) and a melting point of 800 to 10° is to generate a crack in the sealing material and not to generate a crack in the solid electrolyte at the operating temperature (800 to1100 °C) of a solid electrolyte fuel cell. In addition, SnO_2 particles exist in the condition of being dispersed in the glass.

[0010] The sealing material of this invention is not affected under stress by generating a crack in itself so that it prevents generation of the crack in the solid electrolyte. When it is used again, however, a crack is disappeared by being heated and melted so that it can be used as a sealing material again.

[0011] If a sealing material in which SnO_2 with a mean particle diameter of 20 micrometers is added by 10 capacity % in common glass (thermal expansion coefficient: $9.6x10^{-6}$/°C) is used in this invention as an example of the sealing materials used in this invention, the flexural strength is about 2.8 kgf/cm^2.

[0012] The photograph of the microstructure of the sealing material of this

invention taken by an optical microscope (magnifications: 500 times) is shown in FIG 1.

[0013]

[Example] The experiment on the sealing material used for the solid electrolyte fuel cell of this invention has performed using PbO-Al_2O_3-SiO_2 glass as a matrix. The experimental result will be described as follows.

[0014] Effect of the thermal expansion coefficient of a sealing material on a solid electrolyte (8mol% $Y_2O_3ZrO_2$) (Table 1)

The sealing material in which SnO_2 with mean particle diameter of 30 micrometers and thermal expansion coefficient of $4x10^{-6}$/°C is dispersed by 20 capacity % in the sealing material matrix having thermal expansion coefficient of $4x10^{-6}$/°C, $6x10^{-6}$/°C, and $8x10^{-6}$/°C respectively is applied as a sealing material of FIG. 1. After checking the leakage of the sealing at 1000°C, descending a temperature and drawing the solid electrolyte out oft the furnace and observed if the crack had occurred or not. Subsequently put it back to the furnace and raise temperature and checke the sealing at 1000°C again. This result is shown in Table 1.

[Table 1]

Thermal expansion coefficient of a sealing material	$4x10^{-6}$/°C	$6x10^{-6}$/°C	$8x10^{-6}$/°C
Thermal expansion coefficient of a sealing material - Thermal expansion coefficient of a dispersed particle	o	$2x10^{-6}$/°C	$4x10^{-6}$/°C
Sealing at a high temperature	o	o	o

Sealing after descending a temperature	Crack was found in the solid electrolyte	Crack was found in the sealing material	Crack was found in the sealing material
Sealing after re-raising a temperature	X	o	o
Overall assessment	X	o	o

[0015] From the above result, we founded that a crack does not occur in a solid electrolyte when the thermal expansion coefficient of a sealing material matrix is large, and a difference of the thermal expansion coefficient of the sealing material matrix and a dispersed particle material is more than $2x10^{-6}/°C$.

[0016] Effect of the diameter of the particles dispersed in the sealing material with the generation of the crack in a solid electrolyte (Table 2)

The sealing material in which SnO_2 with mean particle diameter of 5, 10, 30, 250, 500, and 750 micrometers and thermal expansion coefficient of $4x10^{-6}/°C$ is dispersed by 20 capacity % in the sealing material matrix having thermal expansion coefficient of $8x10^{-6}/°C$ respectively is applied as a sealing material of FIG. 1. After checking the leakage of the sealing at

1000°C, the temperature was lowered and the solid electrolyte was drawn out of the furnace and was observed if the crack had occurred or not. Subsequently, the electrolyte was put back into the furnace and temperature was raised before checking the sealing at 1000°C again. This result is shown in Table 2.

[Table 2]

Particle diameter	5	10	30	250	500	750
Sealing at a high temperature	o	o	o	o	o	X
Sealing after descending a temperature	Crack was found in the solid electrolyte	Crack was found in the sealing material	←	←	←	←
Sealing after re-raising a temperature	X	o	o	o	o	X
Overall assessment	X	o	o	o	o	X

[0017] The above result shows that a crack does not occur in a solid electrolyte, if the diameter of a particulate material is 10 to 500 micrometers.

[0018] Effect of the amount of the dispersed particle mixed in a sealing

material on the generation of crack in a solid electrolyte (Table 3)

The sealing material in which SnO_2 with mean particle diameter of 30 micrometers and thermal expansion coefficient of $4x10^{-6}/°C$ is dispersed by 3, 5, 10, 20, 40, and 60 capacity % in the sealing material matrix having thermal expansion coefficient of $8x10^{-6}/°C$ respectively is applied as a sealing material of FIG. 1. After checking the leakage of the sealing at 1000°C, the temperature was lowered and the solid electrolyte was removed from the furnace and was observed if the crack had occurred or not. Subsequently, the electrolyte was put back into the furnace and the temperature was raised before checking the sealing at 1000°C again. This result is shown in Table 2.

[Table 3]

amount of the dispersed particle	3	5	10	20	40	60
Sealing at a high temperature	o	o	o	o	o	X
Sealing after descending a temperature	Crack was found in the solid electrolyte	Crack was found in the sealing material	←	←	←	←
Sealing after re-raising a	X	o	o	o	o	X

temperature						
Overall assessment	X	o	o	o	o	X

[0019] The above result shows that a crack does not occur in a solid electrolyte, if the amount of dispersed particle is 5 to 40 capacity %.

[0020]

[Effect of the Invention] This invention provides a solid electrolyte fuel cell which can prevent the generation of a crack in a solid electrolyte caused by the thermal strain that is generated by the difference of thermal expansion coefficients among those of a sealing material, a dispersed particle and a solid electrolyte causes a distortion among them at the time of raising and descending temperature.

[Brief Description of the Drawings]

FIG.1 is an explanatory view of a solid electrolyte fuel cell.

FIG. 2 is an optical microscope photograph in which the detailed organization of the sealing material used by this invention is shown.

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ALLOY SEPARATOR FOR SOLID ELECTROLYTIC FUEL CELL AND MANUFACTURE OF THE SAME

[Abstract]

PURPOSE: To economically manufacture a separator having high electric conductivity and durability by forming a separator from a heat resisting alloy material, and providing predetermined plating layers by wet plating on required surfaces of the separator, respectively.

CONSTITUTION: Separators 4, 4' are formed from heat resisting alloy material, and a Ni plating layer and a LaCrO3 plating layer are provided by wet plating on the respective surfaces opposite to a fuel electrode 1 and an air electrode 2 of the separators 4, 4'. These plating layers prevent the formation of oxidized films on the opposite surfaces to the respective

electrodes of the separators, and an alloy separator for solid electrolytic fuel battery economically enhanced in electric conductivity and durability is provided.

[Claims]

[Claim 1] An alloy separator for solid electrolytic fuel cell with high electric conductivity, having a solid electrolyte, a fuel electrode, an air electrode, and a separator, comprising:

a separator consisted of a heat resisting alloy material;

a nickel plating layer formed by a wet plating on the surface having fuel electrode of said separator; and

a $LaCrO_3$ plating layer formed by wet plating on the surface having an air electrode.

[Claim 2] The alloy separator for solid electrolyte fuel cell of Claim 1, wherein the plating layers have a thickness between 3 and 30 μm.

[Claim 3] The method of preparing an alloy separator for solid electrolyte fuel cell with high electric conductivity, having a solid electrolyte, a fuel electrode, an air electrode, and a separator, comprising:

forming a separator by using a heat resisting alloy material;

forming a Nickel plating layer by wet plating on the surface of said separator having a fuel electrode; and

forming a $LaCrO_3$ plating layer by oxidizing a LaCr-based plating layer that has been electro-deposited by wet plating on the surface of said separator having an air electrode.

[Title of the invention]

ALLOY SEPARATOR FOR SOLID ELECTROLYTIC FUEL CELL AND MANUFACTURE OF THE SAME

[Detailed Description]

[Field of the Invention] The present invention relates to a solid electrolytic fuel cell, and more particularly to a method of preparing an alloy separator for solid electrolyte fuel cell with high electric conductivity.

[Description of the Prior Art] Traditionally, a number of electrolyte fuel cell that uses the direct current energy obtain by a chemical reaction process between gas that can easily be oxidized, such as hydrogen, and gas that have oxidizing power, such as oxygen. An example of such is a solid electrolyte fuel cell (solid oxide fuel cell) that uses a solid electrolyte that exhibits ionic electric conduction. The above-mentioned cell has advantages of: not requiring a higher value metal catalyst such as platinum, having a high efficiency of energy transition, and a low quality fuel such as a coal gas can be used. Moreover, since the cell only in a solid form, no problems arise when treating a liquid electrolyte such as a phosphate electrolyte fuel cell or a melting carbonate fuel cell. Another advantage is that the waste heat of the high reaction temperature of the cell ranging from 800 to 1000 °C can be used.

The above-mentioned solid electrolytic fuel cell can be in a plane or a cylinder shape. For example, as the structure of a single plane-shaped solid electrolytic fuel cell shown in Figure 1, a solid electrolyte (e.g. ZrO_2) plate 3 was inserted between a pair of fuel electrodes 1 and an air electrode 2. Then, they were inserted into separators 4 and 4' that have

numerous pairs of long grooves. Such single cells are connected in a series to become a stack, which can provide a practical electric power supply. Moreover, each unit of the fuel cells is separated by the separator 4, which has a function of providing an electrical connection between the fuel cells connected in a series and a function of supplying a pathway for reactant gases (fuel gas and air).

In general, the electrolyte plate 3 is a sintered body, such as a stabilized oxide zirconium; the fuel electrode (anode) 1 is formed of a sintered body of porous nickel; and the air electrode (cathode) 2 is consisted mainly of sintered body of perovskite oxide. Hydrogen is introduced between the fuel electrode 1 and the separator 4 and oxygen and air are introduced between the air electrode 2 and the separator 4', thereby producing electromotive force by the reactions as follows.

Air electrode (reaction on the surface of the electrolyte):

$O_2 + 4e \rightarrow 20-2$

Fuel electrode (reaction on the surface of the electrolyte):

$2H_2 + 2O-2 \rightarrow 2H_2O + 4e$

The separators 4 and 4' is ordinarily formed of ceramic heat resisting alloy and are provided in an orthogonal structure. The opposite plates of the separators 4 and 4' are consisted of multiple long grooves that act as an air or a fuel pathway, to which air or fuel is supplied. As a material for the separators 4 and 4', $LaCrO_3$-based ceramic, such as $LaCrO_3$, Mg-added $LaCrO_3$, Sr-added $LacRO_3$, or heat resisting alloy, such as Fe-Cr based, Fe-

Cr-Ni based, Ni-Cr based, Ni-Cr-Mo based, Fe-Al based, and Fe-Cr-Al based materials are now in trials to be used.

[Object of the Invention]

As described above, the separator needs to achieve an enhanced function of electrical connection between the cells and form a pathway for the passage of fuel and air from the electrode plates. Thus, not only a good electric conductivity is necessary, but also, keeping air separate from fuel gas is necessary. However, because the above-mentioned heat resisting alloy separator is used at a high temperature surrounding 1000 °C, an oxide film (Cr_2O_3, Al_2O_3, SiO_2, etc.) that have the oxides that are based on parent metals (iron or nickel, etc.) and alloy elements as the main structure are both formed. As a result, the electrical conductivity is decreased, and the electrical connection between the electric cells is damaged. Moreover, due to the formation of a thick film at the side of the air electrode, the cell (air electrode/electrolyte/fuel electrode) is destroyed.

Therefore, in order to hinder the formation of the films and to prevent the decrease in the electric conductivity, $LaCrO_3$ based, $LaMnO_3$ based and $LaCoO_3$ based materials were coated using the metal spraying or the slurry coating methods. However, since a fine film could not be easily achieved by using those methods, oxidation of the separator could not be prevented.

[Means to Solve the Problem] In order to prevent the decrease in the

electric conductivity, the inventors of the present invention found that the oxidation of a separator could be prevented by using a wet plating method of any type of metal or metal oxides, and furthermore, that the method also prevents the decrease in electric conductivity. In other words, the present invention provides an alloy separator for solid electrolytic fuel cell having a fuel electrode, an air electrode, and a separator, wherein the separators 4 and 4' are consisted of heat resisting alloy, the fuel electrode 1 of the separator has a nickel plating layer 4a, and the air electrode 2 has a $LaCrO_3$ plating layer 4b by applying a wet plating method. Additionally a method to prepare an alloy separator for solid electrolytic fuel cell having a solid electrolyte, a fuel electrode, an air electrode, and a separator, characterized in making the separator using heat resisting alloy, forming a nickel plating layer on the fuel electrode side of said separator, and forming a $LaCrO_3$ plating layer by oxidizing LaCr-based plating layer, which is electro-deposited using a wet plating method, on the air electrode side of said separator.

According to the present invention, the thickness of the plating layers is preferably 3 to 30 μm and a nickel plating is formed on the fuel electrode using the wet plating method. Moreover, a $LaCrO_3$ plating layer on the air electrode is formed by plating LaCr followed by an oxidation treatment under a real operating condition. If the plating layer is less than 3 μm thick, the prevention of the oxidation is less effective. Furthermore, if the plating layer is more than 30 μm thick, the resistance is enhanced. Therefore, the electrical connection function is prevented enough at a

thickness between 3 to 30 μm.

Moreover, a good result could also be achieved by using cobalt plating instead of the nickel plating. For $LaCrO_3$, it is preferable to use, other than $LaCrO_3$, $La_{0.9}Mg_{0.1}$ CrO_3, $La_{0.9}Sr_{0.1}$ CrO_3. Furthermore, the same wet plating method can be used.

The sectional structure of the separator can be in the form of one body that has long grooves on both of the fuel electrode side and the air electrode side, an example of which is shown in Figure 2 (A); a three part-type structure having a fuel electrode part, an air electrode part and a heat resisting alloy sandwiched therebetween as shown in Figure 2 (B); and a two part-type structure having a fuel electrode plate and an air electrode plate as shown in Figure 2 (C). In addition, in the figure, 4a is the nickel plating layer and 4b is $LaCrO_3$ plating layer.

[Example] The following is an example of the present invention described in detail.

Ni-Cr-Mo alloy, nickel layer for the fuel electrode, and $LaCrO_3$ layer for the air electrode were used for an alloy separator. For the nickel layer, nickel sulfate ($NiSO_4 \cdot 6\ H_2O$) bath at 2 to 10 A/dm^2 current density and 20 to 30 μm thickness was used to be electro-deposited. For $LaCrO_3$ layer, [$(NH_4)_2$ Cr_2O_7 + $La(NO_3)_3$] bath was used to electro-deposit at an electrical potential (-2.0 V to -1.5 V c sSCE), followed by forming a film having several μm per 1 La/Cr molar ratio and undergoing oxidation between 700

°C to 1000 °C under air.

Figure 3 shows the changes in the generating capacity over a period of time when the alloy separator thusly obtained was used for a solid electrolytic fuel cell. In addition, the same figure also shows the results when an alloy separator without the plating layer.

As shown in the figure, comparing with the alloy separator without the plating layer, the magnitude of the decrease in capacity of the plated alloy separators was much less after a long period of operation. When the alloy separators were observed after the operation, the alloy separator that were plated was seldom changed, while the one without the plating layer showed thick oxide film formed on it. The little degradation of the function of the plated alloy separator was due to a small amount of increase in electric resistance caused by controlled formation of oxide films.

[Effect of the Invention] As explained above, the alloy separator of the present invention prevents the decrease in the electrical connection function at a low cost, and provides a solid electrolytic fuel cell that contains such separator, thereby providing an advantageous electric cell whose capacity does not decrease over a continuous use.

[Brief Description of the Drawing]

[Fig. 1] A perspective exploded illustration of a solid electrolytic fuel cell.

[Fig. 2] A structural sectional view of each type of the separators for a plane-shaped solid electrolytic fuel cell according to the example.

[Fig. 3] A graph showing the changes in the generating capacity over a period of time when the alloy separator with and without plating were used for a solid electrolytic fuel cell.

[Explanation of the References] 1: Fuel Electrode, 2: Air Electrode, 3: Solid Electrolyte Plate, 4, 4': Separator, 4a: Nickel Plating Layer, 4b: $LaCrO_3$ Plating Layer